

Natural attenuation of benzene at an industrial site as evidenced by isotope analysis

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Site description

The polluted site investigated is a fuel depot in the harbour of Amsterdam, which is contaminated with TPH and BTEX and at some places LNAPLs are present. In 1995, benzene was found to be the main pollutant in the middle-deep layer (3-6m-bgs, concentrations up to 6.000 µg/L). The peat layer underlying the middle-deep layer (13-14 m-bgs) and the deeper aquifer were only slightly contaminated.

In 1999 a new site investigation was performed to assess the potential of natural attenuation for the middle-deep groundwater. The aim of this investigation was to confirm that anaerobic biodegradation is reducing the benzene pollution in the middle-deep layer. To realise this, two types of isotope analysis have been applied:

1. Compound specific stable carbon isotope analysis of benzene to proof anaerobic biodegradation.
2. Tritium (³H) analysis to determine the age of the infiltrating groundwater.

Results

The 1999 data show a clear reduction of BTEX concentrations in almost all polluted observation wells over the last four years, limiting the pollution in this layer to benzene in only one of the two originally contaminated spots. Remarkably, the highest benzene concentrations at this spot were observed at the bottom of the layer (2000-10.000 µg/L at 10-12 m bgs), whereas the top of the layer displayed much lower benzene concentrations (10-30 µg/L at 6-9 m-bgs).

The middle-deep layer was found to be anoxic and contained no significant amounts of nitrate and Fe²⁺. Based on sulphate concentrations, sulphate reduction was concluded to occur. Methane was not measured on this site, but on sites nearby methanogenesis was found to occur naturally.

Chloride analysis showed the saltwater/freshwater interface to occur generally at approximately 8-9 m bgs. At the two contaminated spots, however, the interface was found at a depth of 13-14 m bgs; the bottom of the middle-deep layer. Based on this, it was concluded that the two pollutions in the middle-deep layer were caused by increased vertical groundwater transport, possibly due to the presence of anthropogenic drains in the clay layer.

Based on the above results, it was concluded that biodegradation is preventing the migration of toluene, ethylbenzene and xylenes from the top layer to the middle-deep layer. Moreover, the possibility exists that anaerobic benzene degradation is limiting further spreading of benzene. This was unexpected, as the anaerobic degradation of benzene is still a controversial issue.

Compound-specific stable carbon isotope analysis on groundwater samples from the top zone (source) and the middle-deep zone (plume) revealed the benzene in the plume to contain significantly more of the ^{13}C -isotope ($\delta^{13}\text{C} = -24,0\text{‰}$ PDB) than the benzene in the source zone ($\delta^{13}\text{C} = -28,0\text{‰}$ PDB). This significant carbon isotope shift from source to plume is considered a strong indication for anaerobic benzene degradation.

The vertical infiltration was studied using tritium analysis to determine the age of the infiltrating groundwater (see Figure 1). The results show a steady vertical infiltration pattern in the middle-deep zone, implying the benzene pollution at the bottom of the middle-deep layer to be the front of an old plume, which is now disconnected from the source in the top zone. Moreover, it was found that the peat layer at 13-14 m-bgs is functioning as a reasonably effective hydrological barrier, limiting the influence of the increased vertical infiltration to this depth.

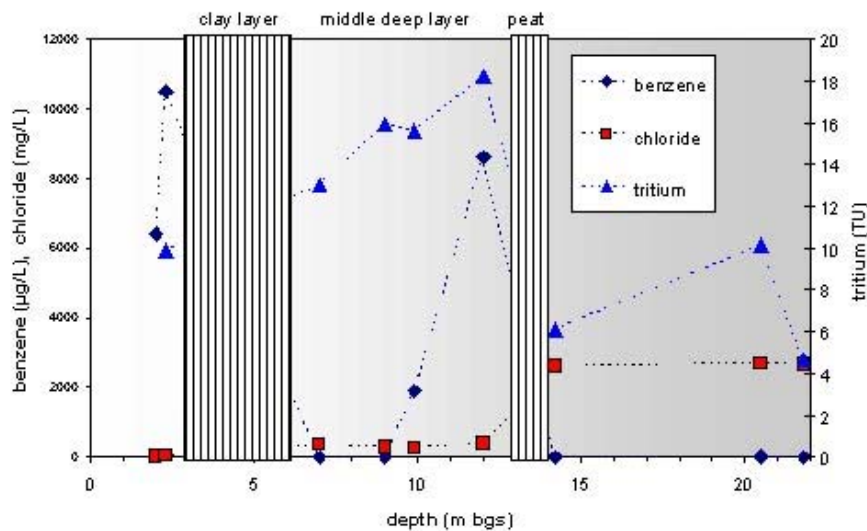


Figure 1: Vertical profile of benzene, chloride and tritium at the location of the benzene contamination in the middle-deep layer

Conclusions

At the site, it was found that for all BTEX compounds the vertical migration from the heavily polluted top zone to the middle-deep groundwater is prevented by (anaerobic) biodegradation. The benzene present at the bottom of the middle-deep layer seems to be the front of the old BTEX-plume, which has not yet been degraded completely and is now disconnected from the source.

Isotope analysis has shown to be a valuable tool in assessment of natural attenuation. Compound specific stable carbon isotope analysis provided a strong indication of anaerobic benzene degradation, whereas tritium analysis confirmed the local groundwater flow pattern, needed to interpret the concentration profiles.